Short communication

Triclinic Na$_{2-x}$Fe$_{1+x/2}$P$_2$O$_7$/C glass-ceramics with high current density performance for sodium ion battery

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HIGHLIGHTS

► We successfully prepared triclinic Na$_{2-x}$Fe$_{1+x/2}$P$_2$O$_7$/C composite by glass-ceramics route.
► Even in 2 μm grain the Na$_{2-x}$Fe$_{1+x/2}$P$_2$O$_7$/C exhibits 86 mAh g^{-1} discharge capacity.
► It is noteworthy of good cyclablity and possible fast ion diffusion.

ARTICLE INFO

ABSTRACT

Triclinic Na$_{2-x}$Fe$_{1+x/2}$P$_2$O$_7$/C composite was prepared by glass-ceramics method. We found that Na$_{2-x}$Fe$_{1+x/2}$P$_2$O$_7$/C composite can be used as cathode active materials for Sodium ion battery with high current density rate performance over 10C (2 mA cm^{-2}) condition and stable electrochemical cycle performance. A 2 μm glass precursor powder in composition of Na$_{2-x}$Fe$_{1+x/2}$P$_2$O$_7$ ($x = 0$–0.44) was crystallized in tubular furnace around 600 °C with carbon source to reduce iron valence state and to coat grain surface with carbon. By means of charge–discharge testing Na$_2$FeP$_2$O$_7$/C composite exhibits 86 mAh g^{-1} (253 Wh kg^{-1}) as reversible discharge energy density that is half amount of that for LiFePO$_4$, however in 10C condition they kept 45 mAh g^{-1} (110 Wh kg^{-1}) even in 2 μm grain size.

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1. Introduction

Recently, poly-anion based LiFePO$_4$ has been much attracted because of its remarkable electrochemical storage properties for the next generation lithium ion secondary battery [1]. LiFePO$_4$ has superior thermal and electrochemical stability compared with conventional LiCoO$_2$, LiMn$_2$O$_4$ cathode materials. The capacity of battery package in electrical vehicle (EV) requires over than 10 kWh, therefore pretty much lithium resources will be required. However, lithium resources are unevenly distributed in the world hence lithium metal is classified as rare-metal resource. In near future the problem concern about materials cost must be happening. On the other hand the other alkaline and alkaline earth ion based secondary batteries are proposed. Especially sodium is being just under the lithium in periodic table and exhibits higher voltage (2.7 V for Na/Na$^+$) after lithium (3.03 V for Li/Li$^+$).

Some articles concern about cathode materials are reported so far [2–8]. Typically, layered rock salt type α-NaCrO$_2$, which is same as LiCoO$_2$, is known as cathode active materials for sodium ion battery [2]. Although the layered rock salt exhibits good electronic conductivity and sodium ion intercalation, but the use of rare metals prohibits its utilization. Phosphate based maricite NaFePO$_4$, which is same composition in LiFePO$_4$, is not suitable for the cathode materials because of complex poly anion units disturbing sodium ion conduction [3]. Therefore there are only a few poly-anions known to be candidates as cathode. Development of new cathode active materials is needed for the realization of sodium ion battery.

By using crystallization process of glass materials, it is easy to control crystal morphology and size distribution from uniform glass matrix. We are proposing unique technique to fabricate phosphate based cathode materials such as olivine structured LiFePO$_4$ and NASICON structured Li$_3$V$_2$(PO$_4$)$_3$ ceramics by crystallization process from glass precursor [9–13]. Precursor glass has very homogeneous compositional distribution hence we obtained any ferromagnetic byproduct free LiFePO$_4$ which works well even in the high current density condition [12].

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Very recently, we found new cathode candidate $Na_2FeP_2O_7$ triclinic P1-crystal that was fabricated by glass-ceramics process [13]. To keep the Fe^{2+} valence states in crystal structure, it is considered that chemical formula can be written as $Na_{2-x}Fe_{1+x/2}P_2O_7$. Actually, Angenault et al. reported $Na_{3.12}Fe_{2.44}P_4O_{14}$ crystal which fabricated by solid-state reaction has P1-structure [14]. In this paper we found that $Na_{2-x}Fe_{1+x/2}P_2O_7$ glass-ceramics is applicable for the sodium ion battery which requires high-rate performance with good cycle ability for the application to electric vehicles.

2. Experimental procedure

The $Na_{2-x}Fe_{1+x/2}P_2O_7$ precursor glass was fabricated by conventional melt-quenching method. Starting reagents $NaPO_3$ (Nakarai tesque) and α-Fe_2O_3 (Kojyundo chemicals) were mixed and melted in platinum crucible at 1100 °C for 10 min in electric furnace. By pouring melts on the steel plate the black-colored precursor glass was successfully formed. The glass transition temperature and crystallization temperature were determined by differential thermal analysis (DTA, Rigaku TG-8120). Glass powder of which grain size is about 2 μm was obtained by using of planetary ball mill (Fritsch premium line P-7). The glass compositions were determined by ICP spectroscopy (ICP–AES, SII SPS4000). Glass ceramics was prepared by heat treatment in 5%H_2–95%Ar gas flowed tubular electric furnace. To reduce Fe^{3+} ion in precursor glass 10 wt% citric acid was added with glass powder. The amount of residual carbon content was determined by thermogravimetric analysis (TG-DTA, Rigaku TG-8120). Powder X-ray diffraction (XRD, Rigaku UltimaIV) employing Cu Kα radiation was used to identify the crystalline phase of prepared powders. Morphologies of glass-ceramics/carbon composites were observed by field emission transmission electron microscope (FE-TEM) (JEOL JEM-2100F). The JEM 2100F has a cold field emission electron source operated at an accelerating voltage of 200 kV. The cathode electrodes were fabricated from a mixture of active material, polyvinylidene fluoride (PVDF) and conductive carbon black in a weight ratio of 85:5:10. N-Methylpyrrolidone (NMP) was used to make the slurry of the mixture. After homegenenization, the slurry was coated on a thin aluminum foil and dried at 100 °C for 10 h in a vacuum oven. The electrode was then pressed and disks were punched out as 16 mmφ. The electrochemical cells were prepared using coin type cells. Sodium metal foils were used as anode, and glass filter paper (Advantec Co., GA-100) was used as separator. Test cell was assembled in an argon-filled glove box. The dew point of Ar atmosphere in glove box was kept as −86 °C. The oxygen content was less than 0.33 ppm. The solution of 1 M $NaPF_6$ (Tokyo Kasei Co.) in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v/v, Kishida Chemicals Co.) was used as electrolyte. The cells were examined by using a battery testing system (Hokuto-denko Co.) at charge/discharge current density range from 1/20 (0.01 mA cm^{-2}) to 10C (2 mA cm^{-2}) for the theoretical capacity as 97 mAh g^{-1} between 2.0 and 3.8 V.

3. Results and discussion

Bulk shape black colored glass was obtained in the system of $Na_{2-x}Fe_{1+x/2}P_2O_7$ ($x = 0$–0.44). The glass compositions are listed in Table 1. Fig. 1 shows the results of differential thermo analysis, the glass transition (T_g) is centered at 490 °C and the crystallization peak (T_p) is centered at 590 °C in each composition. The measure of thermal stability for the divitrification is defined as $T_p - T_g$. It is emphasized that thermal stability for the divitrification of precursor glass is larger than that of LiFePO$_4$ ($\sim$50 K) precursor glass [9,10]. The grain size distribution of precursor glass is being

Table 1
Molar ratio of prepared glasses determined by ICP spectroscopy.

x	Na	Fe	P
0	1.94	1.04	2.04
0.22	1.72	1.14	2.04
0.44	1.60	1.17	2.03

around 2 μm respectively by ball mill process. 10 wt% of citric acid was added and mixed well in glass powder. The crystallization was performed in tubular furnace at crystallization temperature for 90 min. The results are shown in Fig. 2. Simulated patterns of P1-type $Na_2FeP_2O_7$ by RIETAN-FP [15] are also shown [13]. Almost same diffraction patterns are observed in each compositions from $x = 0$ to 0.44. It seems that some amount of sodium ion can be replaced with iron in P1-type $Na_{2-x}Fe_{1+x/2}P_2O_7$ ($x = 0$–0.44).

We examine the cathode properties of $Na_{2-x}Fe_{1+x/2}P_2O_7$ in sodium ion battery. The electrochemical reaction of $Na_{2-x}Fe_{1+x/2}P_2O_7$ crystal is expressed as following equation

$$Na_{2-x}Fe_{1+0.5x}^{(II)}P_2O_7 \rightarrow Na_{1-1.5x}Fe_{1+0.5x}^{(III)}P_2O_7 + (1 + 0.5x) \{Na^+ + e^-\}. \tag{1}$$
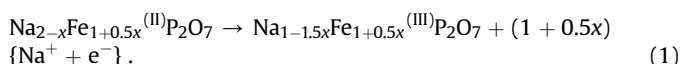
The theoretical capacity of Eq. (1) is estimated as 97 mAh g^{-1} for $x = 0$ and 118 mAh g^{-1} for $x = 0.44$. The charge–discharge curves of $Na_2FeP_2O_7$/C glass-ceramics in various current densities from 0.1C to 10C rate are shown in Fig. 3. The grain size (volume) distribution and high resolution TEM image around the grain surface are also shown. It seems that $Na_2FeP_2O_7$/C grain has 2 μm size covered with few nanometer thickness amorphous carbon layer. The initial discharge capacity is obtained as about 86 mAh g^{-1} (253 Wh kg^{-1}) in 0.05C, which is corresponding to 89% for theoretical capacity. It is considered that reversible electro-chemical reaction is available as shown in Eq. (1). The principal plateau voltage exists at 2.9 V and another plateau was partially observed at 2.5 V. Even in high rate (10C as 2 mA cm^{-2}) 45 mAh g^{-1} (110 Wh kg^{-1}) was obtained. The cycle performance of $Na_2FeP_2O_7$ cathode is shown in Fig. 4. After 50 times the discharge capacity is kept as 96% for the initial discharge. It seems that the electrochemical stability is much better than that of other materials whichever reported [2–8]. We illustrated discharge capacity of various cathode materials as a function of full charge time in Fig. 5. We also indicate the results of LiFePO$_4$ (cutoff voltage 2.5–4.3 V) as a reference [10]. The size distribution of each glass-ceramics composite as well as LiFePO$_4$ reference is same as 2 μm. Although, the actual energy density of $Na_2FeP_2O_7$ at 0.1C
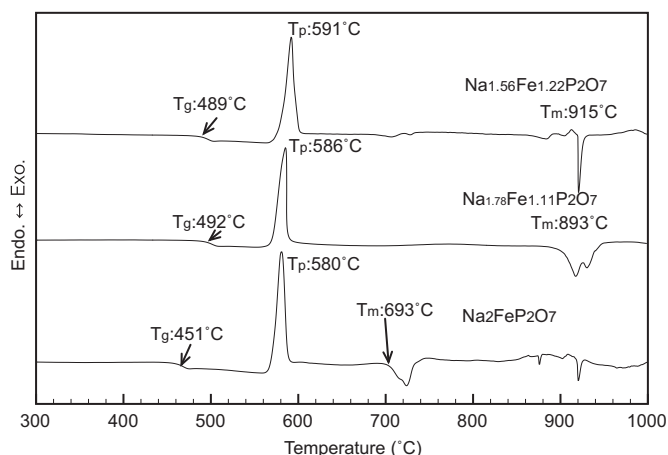
Fig. 1. The DTA patterns of the $Na_{2-x}Fe_{1+0.5x}P_2O_7$ precursor glass.
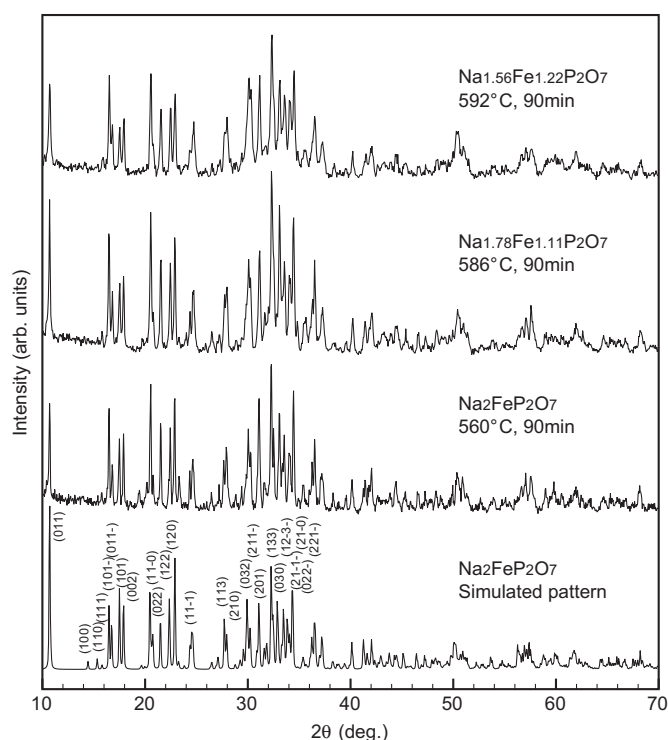
Fig. 2. Powdered XRD patterns of $Na_{2-x}Fe_{1+x/2}P_2O_7$/C glass-ceramics. Simulated pattern for P1-type $Na_2FeP_2O_7$ is also shown.
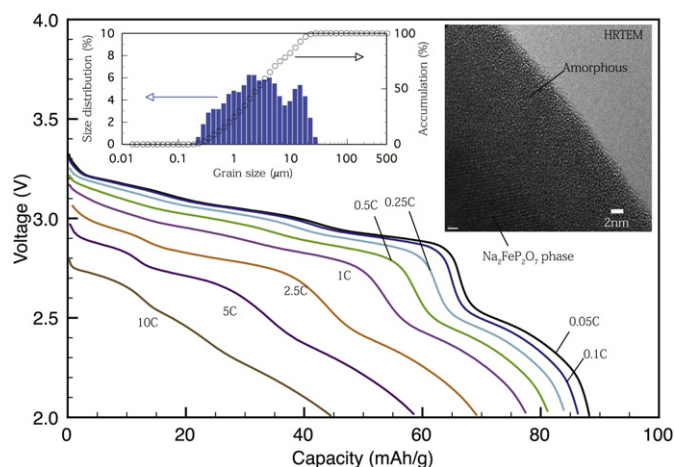

Fig. 3. Discharge profile from 0.05C to 10C, size distribution of glass-ceramics/carbon powder and HR-TEM image around surface in $Na_2FeP_2O_7$/C glass-ceramics.
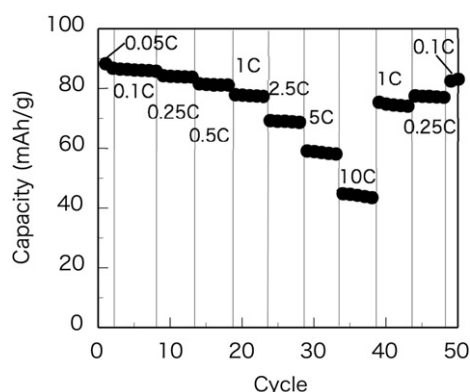

Fig. 4. Cycle performance of $Na_2FeP_2O_7$/C cathode.
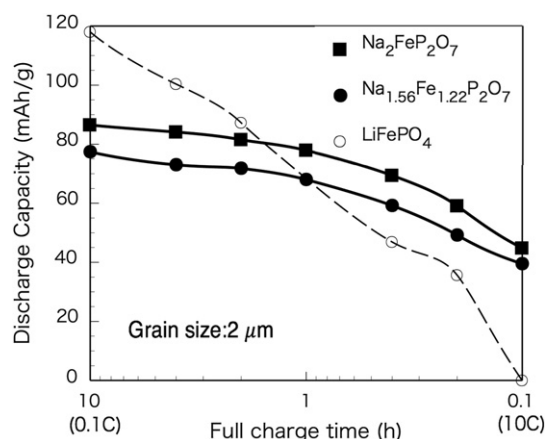
Fig. 5. Discharge capacities of $Na_2FeP_2O_7$/C and $Na_{1.56}Fe_{1.22}P_2O_7$/C glass-ceramics as a function of full charge time. As a reference, the results of $LiFePO_4$ glass-ceramics are also shown.

exhibits a half amount of that in $LiFePO_4$ crystal, however $LiFePO_4$ grains must be much small such as 100 nm or less to work at 10C rate [16]. When the 2 μm size $LiFePO_4$ ceramics no longer does not work at 10C. On the other hand, $Na_2FeP_2O_7$ ceramics readily work as cathode active materials. According to Eq. (1) the theoretical discharge capacity is expected as 118 mAh g^{-1} in $Na_{1.56}Fe_{1.22}P_2O_7$/C composite, however it was almost the same as that of $Na_2FeP_2O_7$. We need the precise structural analysis to clear these phenomena.

4. Conclusions

We fabricated $Na_{2-x}Fe_{1+x/2}P_2O_7$/C composite by glass-ceramics method and reported their cathode performance in sodium ion battery. Actually the theoretical energy density is less than that of lithium ion battery because sodium ion is heavy and large compared that of lithium ion. However, if we obtain unique material which makes large free volume around the guest ions like a $Na_{2-x}Fe_{1+x/2}P_2O_7$, it is expected the realization of high-speed chargeable battery without rare metals.

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